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Molecular Orbital Resonance Theory: Matrix Elements of One-particle Operators

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In the Molecular Orbital Resonance Theory (MORT) each resonance structure is defined as an antisymmetrised product of mutually disjunct bond orbitals. In the present paper expressions for overlaps and matrix elements of one-particle operators between MORT resonance structures are derived.

INTRODUCTION

In the treatment of quantum chemical problems of molecules there are two major ab initio and semi-empirical approaches, namely the molecular orbital (MO) and valence bond (VB) theory.[1-7] The VB theory contains the concept of the resonance which is very helpful in qualitative discussions in organic chemistry. The MO theory however treats one- and two-particle contributions to the energy of the system in the correct order.[8]

There are many attempts to combine the two approaches.[9-11] The so-called Generalized Valence Bond (GVB) theory developed by Goddard and co-workers[9] should be emphasised. It consists in allowing selected electron pairs in the Hartree-Fock wave function

$$\Psi = | \Phi_i, \overline{\Phi}_i, \ldots, \Phi_n, \overline{\Phi}_n |$$

(where Φ_i and $\overline{\Phi}_i$ are spin-α and spin-β molecular orbitals, respectively) to be described in terms of overlapping singly occupied orbitals

$$\Phi_i(1)\,\overline{\Phi}_i(2) \rightarrow [\Phi_{ia}(1)\,\overline{\Phi}_{ib}(2) - \overline{\Phi}_{ia}(1)\,\Phi_{ib}(2)]$$

The concept of localised bonds, such that each bond is described by the use of bond orbitals, is present in the so-called PCILO method.[10] Other authors also discuss possible applications of the chemical bond concept by numerical approximation methods.[11] All these approaches usually sacrifice the very appealing concept of resonance. Recently, a new approach to the treatment of quantum chemical problems was proposed.[8,12] This approach retains the resonance concept of the VB method, but it treats each particular bond in the MO sense. It has been called the Molecular Orbital Resonance Theory (MORT). Even on a very simple level of approximation, which retains only MORT Kekulé struktures and uses the Hückel Hamiltonian, one can obtain quite satisfactory results. For example, by this simple MORT version, the

heats of atomization of conjugated hydrocarbons are reproduced approximately equally well as by the more sophisticated SCF-MO approach.[12] Similarly, heats of atomization of some heteroconjugated systems can be also obtained.[13] Moreover, charge polarisation as well as bond length alternation can be successfully explained for some conjugated hydrocarbons.[8] All these results are obtained on a very simple level of approximation. The use of this approximation amounts to a single diagonalization of a matrix of the order equal to the number of Kekulé structures only. The MORT approach can however be generalised to include more resonance structures and more sophisticated Hamiltonians. It can in fact be made equivalent to the complete configuration interaction (CI) approach. In the forthcoming papers a systematic generalisation and presentation of this method will be given.

This paper can be considered as a first step in this direction. It presents the derivation of matrix elements of one-particle operators between MORT resonance structures.

1. CONFIGURATION INTERACTION SPACE X_n^N AND MORT RESONANCE STRUCTURES

Let $B = \{\chi_i \mid i = 1, \ldots, N\}$ be an orthonormalised set of N one-particle orbitals χ_i. These orbitals can be atomic orbitals (AO's), spin atomic orbitals, molecular orbitals etc. The only requirement is that this set must be orthonormalised. For the sake of reference we will call orbitals χ_i primitive orbitals (PO's). Each subset $D_n \subset B$ of $n \leq N$ primitive orbitals $\chi_{i1}, \ldots, \chi_{in}$ defines a n-particle determinant D_n

$$D_n = |\chi_{i1}, \chi_{i2}, \ldots, \chi_{in}| = \frac{1}{\sqrt{n!}} \sum_P (-1)^P \chi_{i1}(P1) \ldots \chi_{in}(Pn) \tag{1}$$

The summation in (1) is performed over all permutations P of n indices 1, 2, . . ., n. The set of all n-particle determinants (1) is orthonormalised and it spans the configuration interaction (CI) space X_n^N. We define resonance structures in the following way:

Form bond orbitals (BO's) as linear combinations of PO's χ_i

$$\varphi_s = \varphi_{ij} = \frac{1}{\sqrt{2}}(\chi_i + \chi_j) \qquad \text{nonexcited BO}$$

$$\varphi_s^* = \varphi_{ij}^* = \frac{1}{\sqrt{2}}(\chi_i - \chi_j) \qquad \text{excited BO} \tag{2}$$

The term »bond orbital« is taken in analogy with the usual interpretation of these orbitals when χ_i are AO's. However, orbitals φ_s and φ_s^* do not neccessarily have any direct connection with the bond picture. In particular, PO's χ_i and χ_j can correspond to different spin states etc.

We distinguish two types of BO's: excited and nonexcited BO's. The marker (*) denotes an excited BO. For the sake of simplicity we will omit the marker in the notion of the BO, when there is no explicit reference to the excited and nonexcited BO.

We now define:

Definition 1

A n-particle resonance structure (RS) is an antisymmetrised product of n mutually disjuct BO's, i. e.

$$S = \frac{1}{\sqrt{n!}} \sum_P (-1)^P \varphi_{s1}(P1)\, \varphi_{s2}(P2) \ldots \varphi_{sn}(Pn) = \frac{1}{\sqrt{n!}} \sum_P (-1)^P \varphi_{Ps1}(1)\, \varphi_{Ps2}(2) \ldots \varphi_{Psn}(n) \tag{3a}$$

Structure (3a) can be written in the contracted form

$$S = |s_1, s_2, \ldots, s_n\rangle = \frac{1}{\sqrt{n!}} \sum_P (-1)^P |Ps_1, \ldots, Ps_n) \tag{3b}$$

where $|s_1, s_2, \ldots, s_n) = \varphi_{s1}(1)\, \varphi_{s2}(2) \ldots \varphi_{sn}(n)$

is a simple product of BO's. The summation in eqs. (3) is performed over all permutations P of n indices $1, \ldots, n$ (or $s_1, s_2, \ldots, s_n$). By definition, BO's are mutually disjunct if they have no PO in common. A resonance structure can hence be defined only if $2n \leq N$.

One can easily show that the set of all n-particle RS's (3) spans the CI space X_n^N. Each resonance structure satisfying the condition $2n = N$ will be called normal resonance structure (NRS). For the sake of simplicity the corresponding CI space X_n^{2n} will be denoted by X_n.

There is a natural graphical representation of RS's. To each quantum system, for example a π-electron system, a parent graph G is associated. Primitive orbitals are associated with vertices of the graph G. Bond orbital φ_{ij} is represented as a line connecting vertices (i) and (j). If BO is excited (φ_{ij}^*), we put an arrow at the vertex (j) where BO φ_{ij}^* has the phase (—1) (see eq. (2) and Figure 1). In this way one can represent each resonance structure $R \in X_n^N$. A graphical representation of a resonance structure is ambiguous up to the phase (—1). This ambiguity will be treated later.

The condition $2n \leq N$ is necessary in order to define a resonance structure. This condition is however not a serious restriction to generality. Namely, if $2n > N$ one can add $(2n - N)$ dummy vertices to a graph G in order to satisfy the condition $2n = N$. In this way one obtains a graph G′ of which a graph G is a subgraph. All matrix elements taken on dummy vertices and/or connecting them to the graph G should be zero.* An example is given in Figure 2.

A polar structure $S = |12,3\rangle$ is a two-particle state and hence $n = 2$ (Figure 2a). However, a parent graph G has only three vertices and thus $2n = 4 > 3 = N$. We introduce a dummy vertex (4), and a new graph G′ satisfies $2n = N'$ (Figure 2b). Structure S can now be represented as a linear combination of two normal resonance structures (Figure 2c).

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* The introduction of dummy vertices is equivalent to the extension of the orthonormalised base $B = \{\chi_i \mid i = 1, \ldots, N\}$ to the orthonormalised base $B' = \{\chi_i \mid i = 1, \ldots, N'\}$, where $N' = 2n > N$. Dummy orbitals χ_i $(N < i \leq N' = 2n)$ serve only for formal purposes. Graph G′ is now considered to be a parent graph.

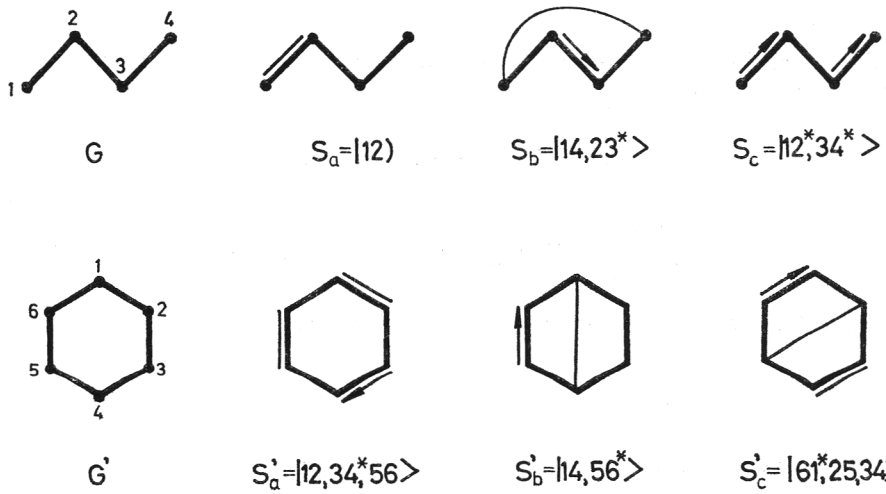


Figure 1. Examples of resonance structures and their graphical representations. G and G' are the corresponding parent graphs. Structures S_b, S_c, S_a' and S_c' are normal resonance structures, while structures S_a and S_b' are not. All BO's contained in a particular RS are mutually disjunct.

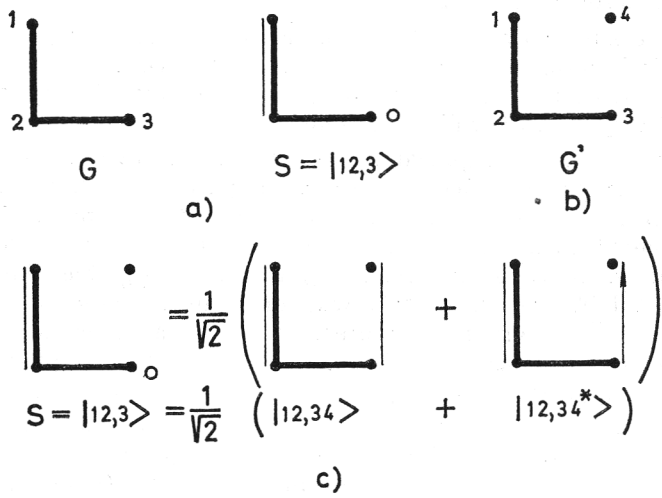


Figure 2. The use of dummy vertices. A polar structure $S = |12,3>$ can be represented as a linear combination of NRS's $S_1 = |12,34>$ and $S_2 = |12,34^*>$, where (4) is a dummy vertex.

Let now $S_a = |s_1, s_2, \ldots, s_n>$ and $S_b = |p_1, p_2, \ldots, p_n>$ be n-particle RS's and let A be one-particle operator. From eqs. (3) it follows

$$S_{ab} = <S_a|S_b> = \sum_P (-1)^P (s_1, \ldots, s_n | Pp_1, \ldots, Pp_n) = \sum_P (-1)^P (s_1|Pp_1)(s_2|Pp_2)\ldots(s_n|Pp_n) \quad (4a)$$

and

$$A_{ab} = <S_a|A|S_b> = \sum_P (-1)^P \sum_{k=1}^{n} (s_1|Pp_1)\ldots(s_k|A|Pp_k)\ldots(s_n|Pp_n) \quad (4b)$$

These relations will be used later in the explicit derivation of overlaps and matrix elements.

2. SUPERPOSITION OF RESONANCE STRUCTURES AND THE NORMAL ORDERING CONVENTION

In order to facilitate the evaluation of overlaps and matrix elements we define the superposition of RS's S_a and S_b:

Definition 2

Superposition of two n-particle resonance structures S_a and S_b is a graph G_{ab}, such that it contains all vertices and all bonds contained in either of these two structures. If a particular bond is contained in both structures, we connect the corresponding vertices in G_{ab} with two bonds. Each bond corresponding to an excited BO is denoted by an arrow, i. e. it is oriented. We use the notation $G_{ab} = S_a \oplus S_b$.

In the theoretical considerations and if there is no explicit reference to excited or nonexcited BO's, we will denote all bonds as being unoriented in the superposition of two structures (see e. g. Figure 4 and Figures 7—12).

One can easily prove

Lemma 1

Superposition $G_{ab} = S_a \oplus S_b$ of resonance structures S_a and S_b consists of disjunct even cycles and/or chains. If in addition RS's S_a and S_b are normal, their superposition contains only disjunct even cycles.

A cycle is even if it contains an even number of bonds. Analogously, we define even chains and odd cycles and chains. There is a special role played by the cycle containing two bonds. Such a cycle results if both structures S_a and S_b contain a BO corresponding to the same bond (s). We call such a cycle a γ-cycle*.

There is some resemblance between the superposition G_{ab} of MORT resonance structures and Rumer diagrams[14] which represent supperpositions of VB resonance structures. There is, however, more information contained in the MORT superposition, since oriented and nonoriented bonds are distinguished, while Rumer diagrams contain only oriented bonds. In addition, each bond in G_{ab} represents one-electron BO, while each bond in a Rumer diagram represents two electrons with paired spins.

Figure 3. illustrates the above lemma.

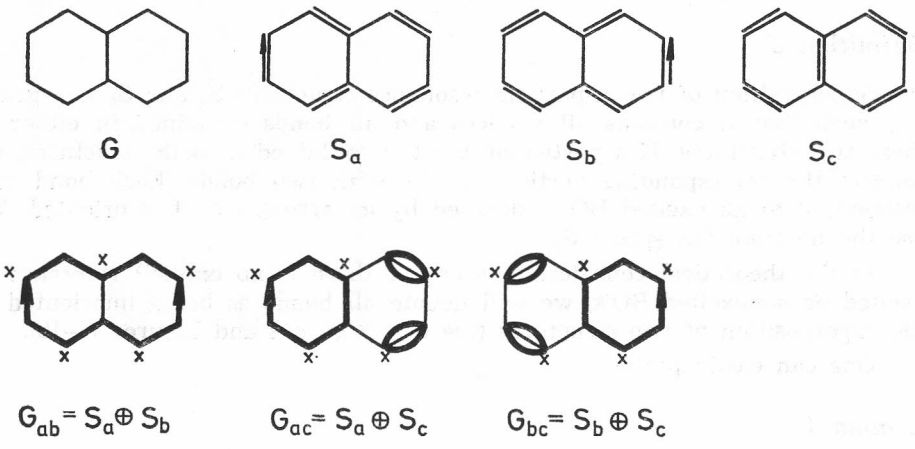
Each excange of two BO's in a given RS changes a phase of this structure by a factor (—1). All matrix elements between different RS's are hence ambiguous up to this phase. One can fix the relative phase between RS's $S_a = |\, s_1, \ldots, s_n >$ and $S_b = |\, p_1, \ldots, p_n >$ in the following way:

1. Form the superposition $G_{ab} = S_a \oplus S_b$ and let $c_1, \ldots, c_\rho$ and $l_1, \ldots, l_\sigma$ be the set of all cycles and chains contained in G_{ab}. If G_{ab} contains more then two odd chains, partition the set of odd chains into pairs in such a way

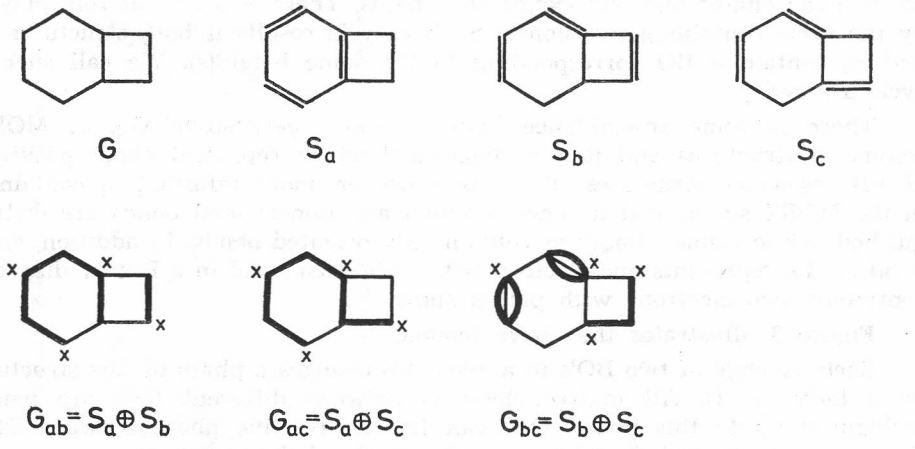
* In graph theory a γ-graph is a graph which contains two vertices connected by a single bond.[15] Here we reserve the term γ-cycle for a graph that consists of two vertices connected by two bonds.

that each pair of two odd chains contains the same number of BO's corresponding to RS's S_a and S_b.

2. Partition all vertices in G_{ab} into sink and source vertices in such a way that no two sinks and no two sources are adjacent to each other. If $l_\mu \in G_{ab}$ is an even chain put sink positions at the ends (terminal positions) of the chain. Sink vertices denote with a cross (x).



a)



b)

Figure 3. Superposition of resonance structures.

a) Structures S_a, S_b and S_c are normal. Superposition G_{ab} is an even cycle, while each of the superpositions G_{ac} and G_{bc} contains three even cycles. Two out of those three cycles are γ-cycles.

b) Structures S_a, S_b and S_c are not normal. Superposition G_{ab} contains two odd chains, superposition G_{ac} contains an even chain, while superposition G_{bc} contains two γ-cycles and an even chain.

3. Fix the phase of each excited BO so that it has the phase (—1) at sink and the phase (+1) at source position.

4. Write BO's $|s_i) \in S_a$ and $|p_i) \in S_b$ in such an order that if BO $|s_i)$ is contained in the cycle $c_\mu \in G_{ab}$, then BO $|p_i)$ is contained in the same cycle. Moreover, BO's $|s_i)$ and $|p_i)$ should lie between the two sink positions on c_μ. Similarly, if BO $|s_i)$ is contained in an even chain l_μ, then BO's $|s_i)$ and $|p_i)$ should lie between the two sink positions on this chain. The same should hold for all BO's contained in the pair $\{l_\mu l_\nu\}$ of two odd chains, except for Bo's $|s_k)$ and $|p_k)$ placed at source end of respective chains (those two BO's can be considered to lie between the two sink positions only if the two terminal source vertices of the respective chains are identified).

For example, in the case of an even cycle, the two RS's can be written in the form (see Figure 4a)

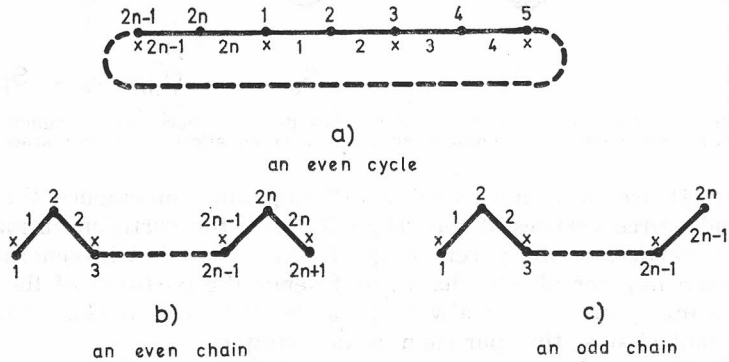


Figure 4. Possible components of the superposition G_{ab} of two RS's. Sink vertices are denoted with a cross (x).

$$S_a = |\ldots;\ 1,\ 3,\ldots,\ 2n-1;\ldots> \qquad (5a)$$
$$S_b = |\ldots;\ 2,\ 4,\ldots,\ 2n;\ldots>$$

or

$$S_a = |\ldots;\ 3,\ 5,\ldots,\ 2n-1,\ 1;\ldots> \qquad (5b)$$
$$S_b = |\ldots;\ 4,\ 6,\ldots,\ 2n,\ 2;\ldots>$$

etc. but not

$$S_a = |\ldots;\ 3,\ 5,\ldots,\ 2n-1,\ 1;\ldots> \qquad (5c)$$
$$S_b = |\ldots;\ 2,\ 4,\ldots,\ 2n-2\ 2n;\ldots>$$

since in this case BO's $|3)$ and $|2)$ in respective structures do not lie between the two sink positions. Similarly, in the case of an even chain one can write (see Figure 4b)

$$S_a = |\ldots;\ 1,\ 3,\ldots,\ 2n-1;\ldots> \qquad (6a)$$
$$S_b = |\ldots;\ 2,\ 4,\ldots,\ 2n-2,\ 2n;\ldots>$$

In the case of an odd chain l_μ one can use the representation (see Figure 4c)

$$S_a = |\ldots;\ 1,\ 3,\ldots,\ 2n-3,\ 2n-1;\ldots> \qquad (6b)$$
$$S_b = |\ldots;\ 2,\ 4,\ldots,\ 2n-2;\ p_k,\ldots>$$

Bond orbital $|s_k) = |2n-1) \in S_a$ is placed at the terminal source vertex of the chain l_μ. This BO is paired with the BO $|p_k) \in S_b$ wich is situated adjacent to the terminal source vertex of the chain l_ν. Chains l_μ and l_ν form a pair of two odd chains.

The above partition into sink and source vertices is always possible since the superposition G_{ab} is by lemma 1 an alternant graph. This partition does not neccessarily coincide with the partition on marked and nonmarked vertices of an alternant parent graph G. For example, in Figure 5 two source positions (5) and (6) are, considered as vertices on the parent graph G, adjacent to

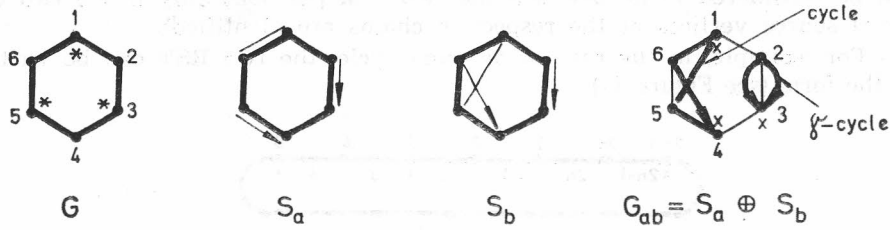


Figure 5. The partition on sink and source vertices does not neccessarily coincides with the partition on marked and nonmarked vertices of an alternant parent graph G.

each other. Hence, it is not possible to bring into coincidence the partition on sink and source vertices of the graph G_{ab} with the partition on marked and nonmarked vertices of the parent graph G. Note also that in general G_{ab} contains an even number of odd chains, and hence the partition of the set of all odd chains into pairs is also always possible. However, if G_{ab} contains more than two odd chains, this partition is not unique.

If RS's S_a and S_b are written in accord with the above conditions, we will say that they satisfy the normal ordering convention. Provided the partition on sink and source vertices is fixed, and if in addition the superposition G_{ab} contains at most two odd chains, then there are n! different representations of n-particle RS's S_a and S_b satisfying the normal ordering convention.

We now define:

Definition 3

The relative phase between two resonance structures S_a and S_b is »normal« if it is fixed according to the normal ordering convention.

It is important to know how much the normal phase between resonance structures S_a and S_b depends on the particular representation satisfying the normal ordering convention. This question is answered by the following.

Theorem 1

1. Normal phase between resonance structures S_a and S_b does not depend on the particular representation satisfying the normal ordering convention, as long as the partition on sink and source vertices and the partition into pairs of odd chains is not changed.

2. Normal phase between resonance structures S_a and S_b does depend on the partition on sink and source vertices and on the partition into pairs of odd chains:

a) Exchange of sink and source vertices in a cycle $c_\mu \in G_{ab}$ changes normal phase by the factor $(-1)^{n_\mu+m_\mu+1}$, where $(2n_\mu)$ is the number of bonds contained in the cycle c_μ, while m_μ is the number of oriented bonds contained in this cycle.

b) Exchange of sink and source vertices in an odd chain l_μ changes normal phase by the factor $(-1)^{n_\mu+m_\mu}$, where $(2n_\mu + 1)$ is the number of bonds contained in the chain l_μ, while m_μ is the number of oriented bonds contained in this chain.

c) In connection with the corollary 1 exchange of two pairs of odd chains is of no immediate interest.

The above Theorem, apart from the point 2c), completely describes the behaviour of the normal phase between the two resonance structures under all transformations admissible by the normal ordering convention. No rule is needed for the exchange of sink and source vertices on an even chain, since such an operation would violate point 2 of the normal ordering convention.

Once the phase between two resonance structures is fixed by a normal ordering convention, and we know from Theorem 1 how this phase changes under all admissible operations, we can proceed to find matrix elements of different operators between those two structures. Accordingly, all the following expressions for overlaps and matrix elements will be derived under the assumption that the phase between the two RS's is normal.

3. FACTORISATION OF OVERLAPS AND MATRIX ELEMENTS OF ONE-PARTICLE OPERATORS

In the Appendix we prove the following.

Theorem 2

Let $S_a = |S_a' S_a''\rangle = |s_1, s_2, \ldots, s_{n'}; s_{n'+1}, \ldots, s_n\rangle$ and $S_b = |S_b' S_b''\rangle = |p_1, p_2, \ldots, p_{n'}; p_{n'+1}, \ldots, p_n\rangle$ be n-particle resonance structures. Let further the superpositions $G_{ab}' = S_a' \oplus S'_b$ and $G_{ab}'' = S_a'' \oplus S_b''$ of the respective substructures be disjunct subgraphs of the superposition $G_{ab} = S_a \oplus S_b$ (G_{ab}' and G_{ab}'' have no vertex in common). Then

$$S_{ab} = \langle S_a | S_b \rangle = \langle S_a' | S_b' \rangle \langle S_a'' | S_b'' \rangle \tag{7a}$$

and

$$A_{ab} = \langle S_a | A | S_b \rangle = \langle S_a' | A | S_b' \rangle \langle S_a'' | S_b'' \rangle + \langle S_a' | S_b' \rangle \langle S_a'' | A | S_b'' \rangle \tag{7b}$$

where A is an arbitrary one-particle operator.

Theorem 2 reduces the calculation of overlap and matrix elements between structures S_a and S_b to the calculation of those quantities between their substructures. The only requirement for the application of this theorem is that the superpositions of respective substructures be disjunct subgraphs of the superposition G_{ab}. Relations (7) can hence be consecutively applied to the substructures S_a', S_b' and S_a'', S_b''. By induction one obtains

$$S_{ab} = \langle S_a | S_b \rangle = \langle S_a^1 | S_b^1 \rangle \ldots \langle S_a^\kappa | S_b^\kappa \rangle \tag{8}$$

$$A_{ab} = \langle S_a | A | S_b \rangle = \sum_{\mu=1}^{\kappa} \langle S_a^1 | S_b^1 \rangle \ldots \langle S_a^\mu | A | S_b^\mu \rangle \ldots \langle S_a^\kappa | S_b^\kappa \rangle \tag{8}$$

where each superposition $G_{ab} = S_a^{\mu} \oplus S_b^{\mu}$ ($\mu = 1, \ldots, \varkappa$) is either a single cycle, or a single even chain, or it contains two odd chains. We hence define.

Definition 4

The superposition G_{ab} of two n-particle resonance structures S_a and S_b is irreducible if it is either a single cycle or a single even chain or if it contains two odd chains.

According to the eqs. (8), in order to find overlap and matrix elements of one-particle operators between arbitrary RS's, it is enough to find those quantities only for those RS's whose superposition is irreducible. In the case of NRS's this is even further simplified since only cycles should be considered. We refer to eqs. (7) and their generalisation (8) as a factorisation Theorem.

One example of the application of this Theorem is given in Figure 6. The superposition G_{ab} contains two irreducible parts, and hence overlap and matrix elements of all one-particle operators can be factorised. Similarly, in Figure 3a superpositions G_{ac} and G_{bc} are reducible and hence the corresponding expressions can be factorised. The superposition G_{bc} in Figure 3b is also reducible, while the superpositions G_{ab} and G_{ac} are not.

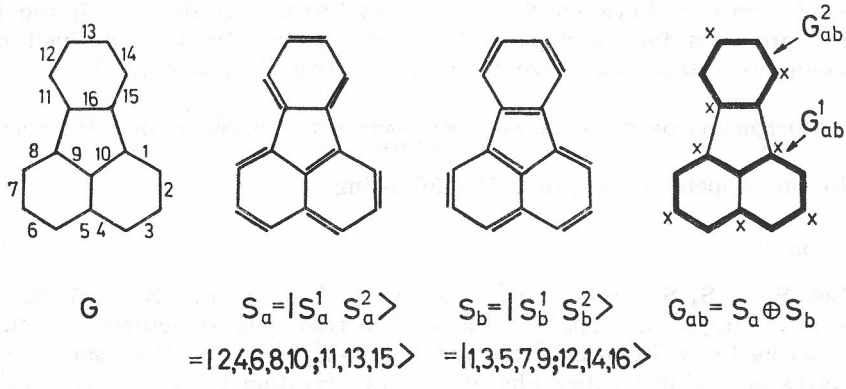


Figure 6. The application of the factorisation Theorem. The superposition G_{ab} contains two cycles and hence it is reducible. Hence $S_{ab} = S_{ab}'\ S_{ab}''$ and $A_{ab} = A_{ab}'\ S_{ab}'' + S_{ab}'\ A_{ab}''$ for any one-particle operator A.

4. ELEMENTARY OPERATORS AND DIFFERENT BOND TYPES

Each one-particle operator can be represented as a linear combination of »elementary« one-particle operators A^{kl} and B^{kl} such that

$$\langle \chi_i \,|\, A^{kl} \,|\, \chi_j \rangle = \delta_{ik}\,\delta_{jl} + \delta_{il}\,\delta_{jk} \quad \text{if } k \neq 1$$
$$\langle \chi_i \,|\, A^{kk} \,|\, \chi_j \rangle = \delta_{ik}\,\delta_{jk} \tag{9a}$$

and

$$\langle \chi_i \,|\, B^{kl} \,|\, \chi_j \rangle = \sqrt{-1}\,(\delta_{ik}\,\delta_{jl} - \delta_{il}\,\delta_{jk}) \tag{9b}$$

i. e. in the base of PO's χ_i all the matrix elements of operators A^{kl} and B^{kl} vanish, except matrix element connecting PO's χ_k and χ_l.

There is a simple connection between elementary operators as defined above and creation and annihilation operators. If a_i^+ and a_i are creation and annihilation operators associated with the PO χ_i, then

$$A^{kl} = A^{lk} = a_k^+ a_l + a_l^+ a_k \quad \text{if } k \neq l$$
$$A^{kk} = A^k = a_k^+ a_k \tag{10}$$
$$B^{lk} = -B^{kl} = i\,(a_k^+ a_l - a_l^+ a_k)$$

Operators A^{kl} are real, while operators B^{kl} are imaginary. We will explicitely give only the rules for the evalution of matrix elements of real elementary operators in the base of RS's. Real operators are by far the most important in quantum chemistry. For example, each velocity independent Hamiltonian is a real operator. Hence, we will by an elementary operator mean a real elementary operator, unless otherwise specified.

One can distinguish two types of elementary operators.

Definition 5

a) If $k \neq l$ operator A^{kl} is a bond operator. We write $A^{kl} = A^{lk} = A^s$, where (s) = (kl).

b) Otherwise, i. e. if $k = l$, we call the operator A^{kk} a vertex operator. We write $A^{kk} = A^k$.

With respect to the superposition G_{ab} of RS's S_a and S_b one can further differentiate bond operators into additional subtypes:

Definition 6

Let G_{ab} be the superposition of RS's S_a and S_b.

a) Bond operator $A^s = A^{kl}$ is »internal« if vertices (k) and (l) are contained in the same connected subgraph of the graph G_{ab} (i. e. either in the same cycle $c_\mu \in G_{ab}$ or in the same chain $l_\mu \in G_{ab}$). Otherwise it is external.

b) Bond operator $A^s = A^{kl}$ is »trans-bridge« if vertices (k) and (l) are either both sink or both source. It is »cis-bridge« if one of those vertices is sink and another source.

c) If a bond (s) = (kl) is contained in the superposition G_{ab}, i. e. if it is a part of either a cycle $c_\mu \in B_{ab}$; or of a chain $l_\mu \in G_{ab}$, bond operator A^s is »normal«. A normal bond operator is a special case of a cis-bridge bond operator.

Analogously one can define different bonds to be normal, cis-bridge, trans-bridge, internal and external. For example, in Figure 7. the superposition G_{ab} consists of an even cycle and an even chain. Bonds (s) and (s′) are normal, bonds (s), (s′), (p) and (p′) are cis-bridge, while bonds (r) and (r′) are trans-bridge. Also, bonds (s) (p), (r) and (s′) are internal, while bonds (p′) and (r′) are external.

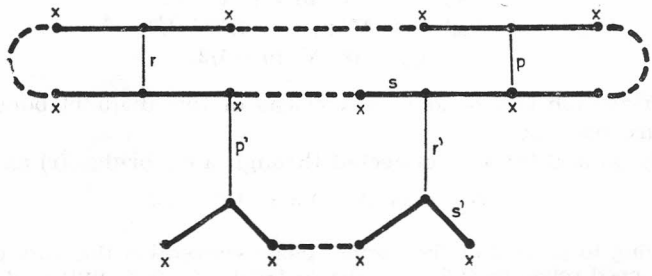


Figure 7 Examples of different bond types.

5. OVERLAP AND MATRIX ELEMENTS OF ELEMENTARY OPERATORS BETWEEN RESONANCE STRUCTURES WHOSE SUPERPOSITION IS IRREDUCIBLE

Consider first the simplest case when resonance structures S_a and S_b are reduced to a single BO. Following cases are possible (Figure 8.):

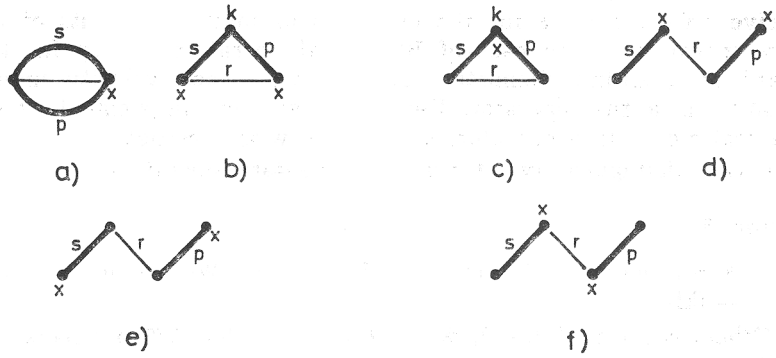


Figure 8. Different types of the superposition of two BO's. Case c) violates point 2. of the normal phase convention, but it is needed in order to evaluate matrix elements between arbitrary resonance structures. Cases d), e) and f) are identical apart from the external bond connecting two odd chains.

1) Superposition $G_{ab} = |s) \oplus |p)$ is a γ-cycle (Figure 8a)

$$S_{ab} = (s \mid p) = [1 + (-1)^m]/2 \tag{11a}$$

$$A_{ab}{}^k = (s \mid A^k \mid p) = \begin{cases} 1/2 & (k) \in G_{ab} \text{ is a source vertex} \\ (-1)^m\ 1/2 & (k) \in G_{ab} \text{ is a sink vertex} \end{cases} \tag{11b}$$

$$A_{ab}{}^s = (s \mid A^s \mid p) = (-1)^{\mathrm{Sgn}(s)}\,[1 + (-1)^m]/2 \tag{11c}$$

2) Superposition $G_{ab} = |s) \oplus |p)$ is an even chain. Vertex (k) common to bonds (s) and (p) is either a source or a sink vertex:

a) Vertex (k) is a source vertex (Figure 8b)

$$\begin{aligned} S_{ab} &= (s \mid p) = 1/2 \\ A_{ab}{}^k &= (s \mid A^k \mid p) = 1/2 \\ A_{ab}{}^s &= (s \mid A^s \mid p) = (-1)^{\mathrm{Sgn}(s)}\ 1/2 \\ A_{ab}{}^r &= (s \mid A^r \mid p) = (-1)^m\ 1/2 \end{aligned} \tag{12a}$$

b) Vertex (k) is a sink vertex (Figure 8c)*

$$\begin{aligned} S_{ab} &= (s \mid p) = (-1)^m\ 1/2 \\ A_{ab}{}^k &= (s \mid A^k \mid p) = (-1)^m\ 1/2 \\ A_{ab}{}^s &= (s \mid A^s \mid p) = (-1)^{\mathrm{Sgn}(p)}\ 1/2 \\ A_{ab}{}^r &= (s \mid A^r \mid p) = 1/2 \end{aligned} \tag{12b}$$

3) Superposition $G_{ab} = |s) \oplus |p)$ consists of two disjunct bonds (s) and (p). Two cases are possible.

a) Bonds (s) and (p) are connected through a cis-bridge (r) as in Figure 8d:

$$A_{ab}{}^r = (s \mid A^r \mid p) = (-1)^{\mathrm{Sgn}(s)}\ 1/2 \tag{13}$$

---

* According to point 2 of the normal phase convention this case does not occur. However, we need relations (12b) in order to facilitate the evalution of more complex matrix elements (see e. g. proff of the Theorem 3 in the Appendix).

b) Bonds (s) and (p) are connected through a trans-bridge (r) (Figures 8e and 8f):

$$A_{ab}{}^{r} = (s \mid A^{r} \mid p) = \begin{cases} 1/2 & \text{bond (r) connects two source vertices} \\ (-1)^{m}\, 1/2 & \text{bond (r) connects two sink vertices} \end{cases} \tag{14}$$

The above relations follow from the eq. (2) and from the definitions (9a) of elementary operators A^{kl}. In those relations m is the number of oriented bonds contained in the superposition G_{ab}, while Sgn(s) = 1 if BO | s) is excited and Sgn (s) = O otherwise. Matrix elements not listed in the above relations are either deducible from them by symmetry considerations, or if not, they are zero. Using these relations we prove in the Appendix the following three Theorems concerning overlaps and matrix elements of elementary operators A^{kl} between resonance structures whose superposition is irreducible:

Theorem 3

Let the superposition G_{ab} of two n-particle resonance structures S_a and S_b be a single cycle. Further, let A be an elementary operator and let m be the number of oriented bonds contained in the cycle G_{ab} (see Figure 9.). Then:

1. Overlap S_{ab} equals:

$$S_{ab} = \langle S_a \mid S_b \rangle = [1 + (-1)^{n+m+1}]/2^{n} \tag{15}$$

2. If $A = A^{k}$ is a vertex operator and $(k) \in G_{ab}$:

$$A_{ab}{}^{k} = \langle S_a \mid A^{k} \mid S_b \rangle = \begin{cases} 2^{-n} & \text{(k) is a source vertex} \\ (-1)^{n+m+1}\, 2^{-n} & \text{(k) is a sink vertex} \end{cases} \tag{16}$$

3. If $A = A^{kl} = A^{s}$ is an internal bond operator:

a) Bond (s) is normal

$$A_{ab}{}^{s} = \langle S_a \mid A^{s} \mid S_b \rangle = (-1)^{Sgn(s)}\, [1 + (-1)^{n+m+1}]/2^{n} = (-1)^{Sgn(s)}\, S_{ab} \tag{17}$$

where Sgn (s) = 1 if BO | s) is excited, and Sgn (s) = O otherwise.

b) Bond (s) is a cis-bridge. In this case bond (s) forms two even cycles c′ and c″ on G_{ab} (see Figure 9b). We have

$$A_{ab}{}^{s} = \langle S_a \mid A^{s} \mid S_b \rangle = (-1)^{n'+m'+1}\, [1 + (-1)^{n+m+1}]/2^{n} = (-1)^{n'+m'+1}\, S_{ab} \tag{18}$$

where (2n′) is the number of bonds contained in a cycle c′, while m′ is the number of oriented bonds contained in this cycle.

c) Bond (s) is trans-bridge. In this case bond (s) forms two odd cycles c′ and c″ on G_{ab} (see Figure 9c). We have

$$A_{ab}{}^{s} = \langle S_a \mid A^{s} \mid S_b \rangle = \begin{cases} (-1)^{n'+m'}\, [1 + (-1)^{n+m}]/2^{n} & \text{bond (s) connects two source vertices on } G_{ab} \\ (-1)^{n'+m'+1}\, [1 + (-1)^{n+m}]/2^{n} & \text{bond (s) connects two sink vertices on } G_{ab} \end{cases} \tag{19}$$

where $(2n' + 1)$ is the number of bonds contained in a cycle c', while m' is the number of oriented bonds contained in this cycle.

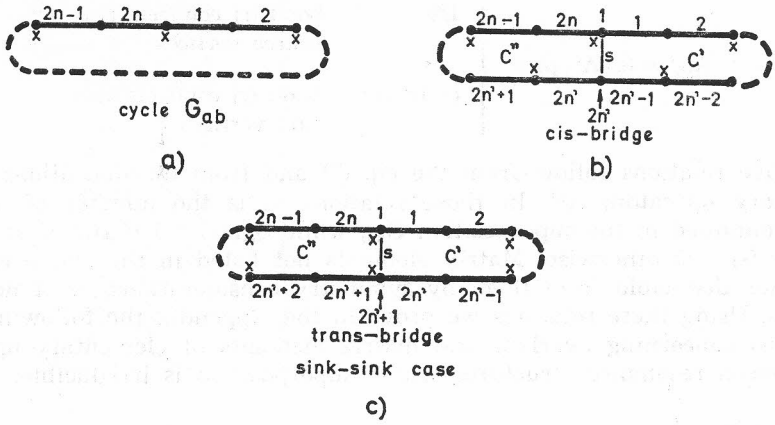


Figure 9. The superposition G_{ab} of resonance structures S_a and S_b is an even cycle. Formulas for overlap and matrix elements of elementary one-particle operators between those two structures are given by Theorem 3.

Theorem 4

Let the superposition G_{ab} of two n-particle resonance structures S_a and S_b be an even chain. Further, let A be an elementary operator and let m be the number of oriented bonds contained in the chain G_{ab} (see Figure 10.). Then:

1. Overlap S_{ab} equals

$$S_{ab} = \langle S_a \mid S_b \rangle = 2^{-n} \tag{20}$$

2. If $A = A^k$ is a vertex operator and $(k) \in G_{ab}$ then:

$$A_{ab}{}^{k} = \langle S_a \mid A^k \mid S_b \rangle = \begin{cases} 2^{-n} = S_{ab} & \text{(k) is a source vertex} \\ O & \text{(k) is a sink vertex} \end{cases} \tag{21}$$

3. If $A = A^{kl} = A^s$ is the internal bond operator:

a) Bond (s) is normal

$$A_{ab}{}^{s} = \langle S_a \mid A^s \mid S_b \rangle = (-1)^{Sgn(s)}/2^n = (-1)^{Sgn(s)}\, S_{ab} \tag{22}$$

b) Bond (s) is cis-bridge (see Figure 10b). In this case bond (s) forms an even cycle c' on G_{ab} and

$$A_{ab}{}^{s} = \langle S_a \mid A^s \mid S_b \rangle = (-1)^{n'+m'+1}/2^n = (-1)^{n'+m'+1}\, S_{ab} \tag{23}$$

where $(2n')$ is the number of bonds in a cycle c', while m' is the number of oriented bonds contained in this cycle.

c) Bond (s) is trans-bridge. In this case bond (s) forms an odd cycle c' on G_{ab} (see Figure 10c). We have

$$A_{ab}{}^{s} = \langle S_a \mid A^s \mid S_b \rangle = \begin{cases} (-1)^{n'+m'}/2^n = (-1)^{n'+m'}\, S_{ab} & \text{bond (s) connects two source vertices on } G_{ab} \\ (-1)^{n'+m'+1}/2^n = (-1)^{n'+m'+1}\, S_{ab} & \text{bond (s) connects two sink vertices on } G_{ab} \end{cases} \tag{24}$$

where $(2n' + 1)$ is the number of bonds contained in the cycle c′, while m′ is the number of oriented bonds contained in this cycle.

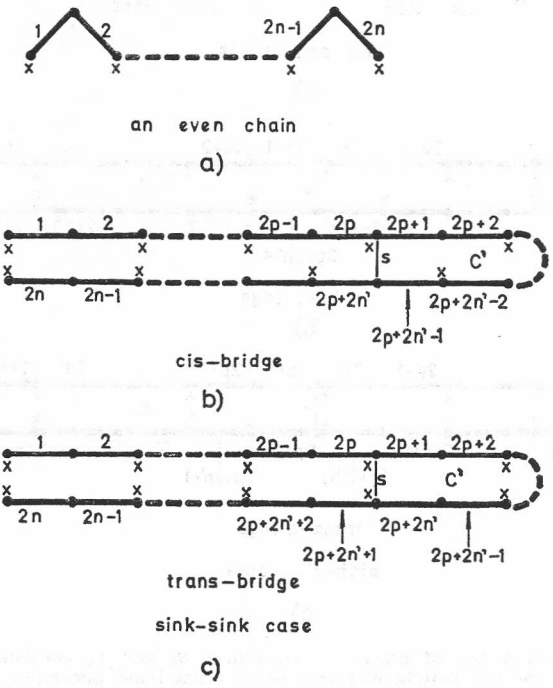


Figure 10. Superposition G_{ab} of resonance structures S_a and S_b is an even chain. Formulas for overlap and matrix elements of elementary operators between those two structures are given by Theorem 4.

Theorem 5

Let the superposition G_{ab} of two n-particle resonance structures S_a and S_b consists of two odd chains. Further, let A be an elementary operator and let m be the number of oriented bonds contained in G_{ab} (see Figure 11.). Then:

1. Overlap and matrix elements of all elementary one-particle operators, except external bridge type operators connecting two chains, are equal zero.

2. Concerning external bridge type operators relations (23) and (24) for cis- and trans-bridge on an even chain remain valid, provided we identify two source terminal-vertices of odd chains l_1 and l_2, thus forming an even chain l (see Figures 11b and 11c). i. e.

a) Bond (s) is external cis-bridge (Figure 11b). In this case bond (s) forms an even cycle c′ on the chain l and

$$A_{ab}^{s} = \langle S_a \mid A^s \mid S_b \rangle = (-1)^{n'+m'+1}/2^n \qquad (25)$$

where $(2n')$ is the number of bonds in a cycle c′, and m′ is the number of oriented bonds in this cycle.

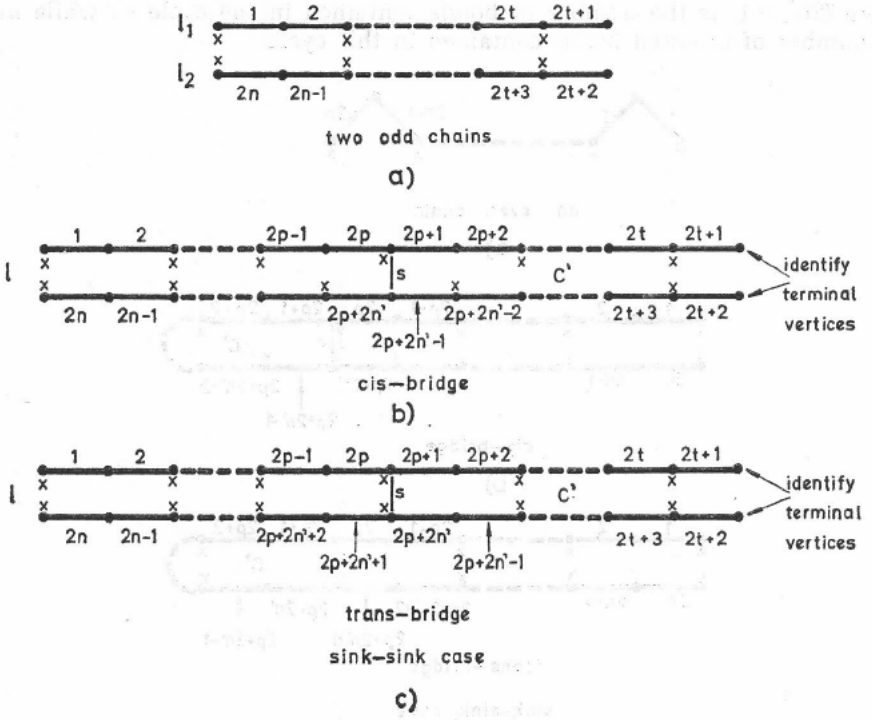


Figure 11. Superposition G_{ab} of resonance structures S_a and S_b consists of two odd chains l_1 and l_2. Formulas for the matrix elements of external bond operators reduce to the corresponding formulas for an even chain, provided two terminal source vertices on chains l_1 and l_2 are identified, thus forming an even chain l. For details see Theorem 5.

b) Bond (s) is external trans-bridge (Figure 11c). In this case bond (s) forms an odd cycle c′ on the chain 1 and

$$A_{ab}{}^{s} = \langle S_a | A^s | S_b \rangle = \begin{cases} (-1)^{n'+m'}/2^n & \text{bond (s) connects two source vertices on } G_{ab} \\ (-1)^{n'+m'+1}/2^n & \text{bond (s) connects two sink vertices on } G_{ab} \end{cases} \tag{26}$$

where $(2n' + 1)$ is the number of bonds contained in the cycle c′, and m′ is the number of oriented bonds contained in this cycle.

Concerning the above Theorems some remarks are necessary:

1. In points 3b) and 3c) of Theorem 3, there is a reference to the number of bonds $(2n')$ and $(2n' + 1)$, respectively, and to the number of oriented bonds m′ in a cycle c′. However, both, cis- and trans-bridge form two cycles, a cycle c′ and a cycle c″. Eqs. (18) and (19) might hence seem to be ill-defined. But this is only apparently so and these equations remain valid if we substitute n″ for n′ and m″ for m′. Which cycle we call cycle c′ and which c″ is of no consequence. This can be shown to be true by direct derivation, but it is

simpler to prove it starting from the very eqs. (18) and (19). Take for example eq. (18). It contains a phase factor $(-1)^{n'+m'+1}$. However, $m' = m - m''$, where m'' is the number of oriented bonds in a cycle c'' (Figure 9b). Also, and since there are two vertices common for cycles c' and c'', we have $2n = 2n' + 2n'' - 2$. Hence $(-1)^{n'+m'+1} = (-1)^{n+m+1+n''+m''+1}$. But now if $(n + m + 1)$ is even this phase reduces to $(-1)^{n''+m''+1}$, if however $(n + m + 1)$ is odd then by (18) matrix element $A_{ab}{}^{s}$ vanishes since $1 + (-1)^{n+m+1} = 0$. Hence $A_{ab}{}^{s} = (-1)^{n''+m''+1}[1 + (-1)^{n+m+1}]/2^{n}$ in both cases. In a similar way one can show that in the eq. (19) n' and m' can be substituted by n'' and m'', respectively.

2. Point 3b) of the same Theorem gives a rule for a matrix element of an elementary operator defined on a cis-bridge. However, a normal bond can be considered to be a special case of a cis-bridge where one of the two cycles c' and c'' reduces to a γ-cycle. If the normal bond is considered to form a γ-cycle, then one bond joining vertices (i) and (j) should correspond to a cis-bridge proper, while another bond joining those two vertices should belong to a superposition G_{ab} (see Figure 12b).

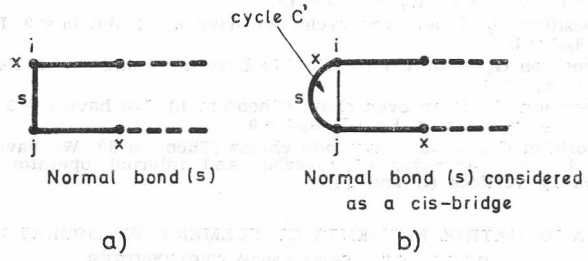


Figure 12. Normal bond (s) can be considered to be a cis-bridge forming a γ-cycle c'. Formulas for matrix elements of normal bond operator can be shown to be a special case of formulas for the matrix elements of cis-bridge operators.

With this convention we have $2n' = 2$ and $m' = \mathrm{Sgn}(s)$. Hence $(-1)^{n'+m'+1} = (-1)^{\mathrm{Sgn}(s)}$ and thus eq. (18) is reduced to eq. (17). The rule for the matrix elements of an operator defined on a normal bond is a special case of a matrix element of an operator defined on a cis-bridge. Similarly, in the case when G_{ab} is an even chain (Theorem 4) eq. (23) reduces to eq. (22) if a cis-bridge degenerates into a normal bond. Hence, with due caution, one can altogether omit the rule concerning matrix elements of a normal bond operator.

3. Notice finally that relations (15), (16) and (17) valid for the case when G_{ab} is an arbitrary cycle, reduce to relations (11) valid for the case when G_{ab} is a γ-cycle if we put $2n = 2$. Under the same condition relations (20)—(24), valid for an arbitrary even chain, reduce to relations (12a), valid for an even chain containing two bonds, and also corresponding relations valid for an arbitrary pair of odd chains reduce to the relations (13) and (14), valid for two odd chains containing one bond each.

Some examples of the application of Theorems 3, 4 and 5 are given in Figure 13.

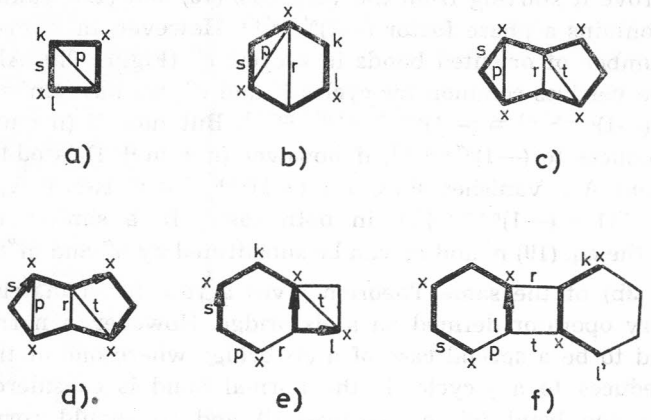


Figure 13. Examples for the application of Theorems 3, 4 and 5.

a) The superposition G_{ab} is an even cycle (Theorem 3.). We have $n = 2$ and $m = 0$. Hence $S_{ab} = A_{ab}{}^{s} = 0$, $A_{ab}{}^{p} = -1/2$, $A_{ab}{}^{k} = -A_{ab}{}^{l} = 1/4$.

b) The superposition G_{ab} is an even cycle (Theorem 3.). We have $n = 3$ and $m = 0$. Hence $S_{ab} = A_{ab}{}^{s} = -A_{ab}{}^{r} = 1/4$, $A_{ab}{}^{p} = 0$, $A_{ab}{}^{k} = A_{ab}{}^{l} = 1/8$.

c) The superposition G_{ab} is an even cycle. We have $n = 4$ and $m = 0$. Hence $S_{ab} = A_{ab}{}^{t} = A_{ab}{}^{s} = 0$, $A_{ab}{}^{p} = A_{ab}{}^{r} = 1/8$.

d) The superposition G_{ab} is an even cycle. We have $n = 4$ and $m = 3$. Hence $S_{ab} = -A_{ab}{}^{s} = -A_{ab}{}^{t} = 1/8$, $A_{ab}{}^{p} = A_{ab}{}^{r} = 0$.

e) The superposition G_{ab} is an even chain (Theorem 4.). We have $n = 3$ and $m = 3$. Hence $S_{ab} = A_{ab}{}^{k} = -A_{ab}{}^{s} = A_{ab}{}^{p} = A_{ab}{}^{r} = A_{ab}{}^{t} = 1/8$, $A_{ab}{}^{l} = 0$.

f) The superposition G_{ab} contains two odd chains (Theorem 5.). We have $n = 4$ and $m = 1$. Hence $S_{ab} = A_{ab}{}^{s} = A_{ab}{}^{p} = A_{ab}{}^{k} = A_{ab}{}^{l} = 0$ (overlap and internal operators). Further $A_{ab}{}^{t} = -A_{ab}{}^{r} = 1/16$ (identify vertices (1) and 1')).

6. OVERLAPS AND MATRIX ELEMENTS OF ELEMENTARY OPERATORS BETWEEN ARBITRARY RESONANCE STRUCTURES

Combining Theorems 3, 4 and 5 with the factorisation Theorem one can now derive overlaps and matrix elements of elementary operators between arbitrary resonance structures. Notice that in relations (15)—(19) related to Theorem 3, the parity of the quantity (n + m) plays an important role. Hence, we define

Definition 7

A cycle $c_\mu \in G_{ab}$ is »passive« if $(n_\mu + m_\mu)$ is even, and it is »active« otherwise. Here $(2n_\mu)$ is the number of BO's contained in the cycle $c_\mu \in G_{ab}$, while m_μ is the number of oriented bonds contained in this cycle.

With the help of this definition one can now formulate a few simple corollaries. Let G_{ab} be the superposition of n-particle resonance structures S_a and S_b and let $c_1, \ldots, c_\varrho$ and $l_1, \ldots, l_\sigma$ be the set of all cycles and chains contained in G_{ab}. Then

Corollary 1

If the superposition G_{ab} contains more then two odd chains overlap and matrix elements of all one-particle operators between these two structures are equal zero.

Corollary 2

Matrix element $A_{ab}{}^{s} = \langle S_a \mid A^s \mid S_b \rangle$ of each bond operator A^s connecting two different irreducible parts of the superposition G_{ab} equals zero.

In particular if bond (s) connects two cycles, or two even chains, or cycle and a chain, the matrix element $A_{ab}{}^{s}$ vanishes.

Corollary 3

Overlap S_{ab} equals

$$S_{ab} = \langle S_a \mid S_b \rangle = \begin{cases} 0 & \text{if } G_{ab} \text{ contains an odd chain} \\ & \text{and/or a passive cycle} \\ 2^{p-n} & \text{otherwise} \end{cases} \tag{27}$$

Corollary 4

Matrix element $A_{ab}{}^{s}$ of a normal bond operator A^s equals

$$A_{ab}{}^{s} = \langle S_a \mid A^s \mid S_b \rangle = (-1)^{Sgn(s)} S_{ab} \tag{28}$$

Corollary 5

Matrix element $A_{ab}{}^{s}$ of internal cis-bridge operator A^s equals

$$A_{ab}{}^{s} = \langle S_a \mid A^s \mid S_b \rangle = (-1)^{n_s+m_s+1} S_{ab} \tag{29}$$

where $(2n_s)$ is the number of bonds in either of the two cycles c_s' and c_s'' formed by a cis-bridge (s) over G_{ab}, and m_s is the number of oriented bonds in this cycle.

Similar expressions can be derived for all other cases.

7. MATRIX ELEMENTS OF IMAGINARY ONE-PARTICLE OPERATORS

So far we gave only the rules for the evalution of matrix elements $A_{ab}{}^{kl} = \langle S_a \mid A^{kl} \mid S_b \rangle$ of real one-particle operators A^{kl} between RS's S_a and S_b. In order to evaluate matrix elements of an arbitrary one-particle operator between RS's S_a and S_b one needs in addition rules for the evalution of matrix elements $B_{ab}{}^{kl} = \langle S_a \mid B^{kl} \mid S_b \rangle$ of imaginary operators B^{kl} between RS's S_a and S_b. As mentioned above, such operators are not so important in quantum chemistry. Hence, and for the sake of restricted space, we will not give here all those matrix elements, but we will rather only outline their derivation. Take e. g. the case when the superposition G_{ab} is a single cycle and operator B^{kl} is an imaginary normal bond operator. Further, let (1) be a source and (k) a sink vertex. The derivation of the matrix element $\langle S_a \mid B^{kl} \mid S_a \rangle$ follows the derivation of the corresponding matrix element $\langle S_a \mid A^{kl} \mid S_b \rangle$ of the real operator A^{kl}. Up to eq. (A8) in the Appendix we have completely parallel expressions. Here however $(1 \mid B^{kl} \mid 2) = -(1 \mid B^{kl} \mid 2n) = i/2$ (see Appendix and eq. (9b)). Hence and from eq. (A8).

$$\langle S_a \mid B^{kl} \mid S_b \rangle = - \langle S_a \mid B^{lk} \mid S_b \rangle = i\,(-1)^{Sgn(s)}\,[1 + (-1)^{n+m}]/2^n \tag{30}$$

This expression should be compared with the corresponding expression (17) for the real operator A^{kl}. Similarily, if B^{kl} is a cis-bridge operator and (k) is a sink vertex one obtains

$$\langle S_a | B^{kl} | S_b \rangle = - \langle S_a | B^{lk} | S_b \rangle = i\,(-1)^{n'+m'+1}\,[1 + (-1)^{n+m}]/2^n \qquad (31)$$

which should be compared with the analogous expression (18) involving the real elementary operator A^{kl}. In the same way one can derive all other matrix elements of imaginary one-particle operators B^{kl} between different resonance structures.

To complete the list of matrix elements one should include two-particle operators as well. Theorems 3, 4 and 5 in connection with the factorisation Theorem form a sufficient base for the development of an elementary theory. We limit here our discussion to the evalution of matrix elements of one--particle operators, while the evalution of the corresponding theory as well as the inclusion of two-particle operators to form a more satisfactory system will be done elsewhere.[16]

CONCLUSION

This paper deals with the evalution of overlaps and matrix elements of one-particle operators between MORT resonance structures. In the first paragraph the MORT resonance structures are defined (Definition 1). The phase of a particular resonance structure, and hence all matrix elements between those structures, are ambiguous up to the factor (—1). In order to lift this ambiguity, a normal phase between two resonance structures is defined (Definition 3). The phase between two resonance structures may be fixed in many different ways, and in particular definition 3 is chosen in order to make this phase invariant to as many different operations as possible (see Theorem 1). Theorem 2 expresses overlap and matrix elements between two resonance structures in terms of overlaps and matrix elements defined on the basis of their substructures. Using the concept of the superposition of two resonance structures one can decompose each pair of structures into »elementary parts«, i. e. such pairs of substructures whose superposition is irreducible in the sense of Definition 4. Finally, the formulas for overlaps and matrix elements between resonance structures whose superposition is irreducible are explicitely given by Theorems 3, 4 and 5.

The method for the calculation of matrix elements outlined here is quite simple and straightforward. The decomposition into smaller parts will prove useful in the further development of the theory.[16] There is some formal resemblance to the calculation of matrix elements in the VB theory. The formulas obtained, as well as the very notion of the resonance structure, are however different in these two approaches.

APPENDIX

Proof of the Theorem 1

If the partition on sink and source vertices, as well as the partition into pairs of odd chains is not changed, then the transition from one to another representation, satisfying normal ordering convention, is accomplished by some permutation P_a of BO's contained in a structure S_a and some permutation P_b of BO's contained in a structure S_b. From point 4 of the normal ordering convention it follows that those two permutations are identical, and hence the relative phase between the two structures does not change. This proves the first part of Theorem 1. Consider now

point 2a). If the role of sink and source vertices is exchanged in the cycle $c_\mu \in G_{ab}$, all excited BO's corresponding to this cycle change sign. This produces the factor $(-1)^{m_\mu}$. In addition, the related BO's in respective structures do not anymore lie between the two sink positions. In order to restore this condition one has to perform a cyclic permutation of n_μ BO's, and this produces the additional factor $(-1)^{n_\mu+1}$. This proves point 2a). In a similar way point 2b) can be proven.

Proof of the Theorem 2

Consider the overlap $\langle S_a \mid S_b \rangle$. According to eq. (4a)

$$\langle S_a \mid S_b \rangle = \sum_P (-1)^P (s_1 \mid Pp_1) \ldots (s_{n'} \mid Pp_{n'}) (s_{n'+1} \mid Pp_{n'+1}) \ldots (s_n \mid Pp_n) \tag{A1}$$

In the relation (A1) the summation is performed over all permutations P of n indices $p_1, p_2, \ldots, p_n$. However, since G_{ab}' and G_{ab}'' are disjunct, overlap $(s_1 \mid Pp_1)$ vanishes whenever BO $\mid Pp_1)$ is contained in the superposition G_{ab}''. Similarly for all other overlaps $(s_2 \mid Pp_2), \ldots, (s_{n'} \mid Pp_{n'})$. Hence

$$\begin{aligned}
&\langle S_a \mid S_b \rangle = \\
&= \sum_{P'} (-1)^{P'} (s_1 \mid P' p_1) \ldots (s_{n'} \mid P' p_{n'}) \sum_{P''} (-1)^{P''} (s_{n'+1} \mid P'' p_{n'+1}) \ldots (s_n \mid P'' p_n) = \\
&= \langle S_a' \mid S_b' \rangle \langle S_a'' \mid S_b'' \rangle
\end{aligned} \tag{A2}$$

Similary, in the case of one-particle operator A

$$\begin{aligned}
&\langle S_a \mid A \mid S_b \rangle = \sum_P (-1)^P \sum_{k=1}^{n} (s_1 \mid Pp_1) \ldots (s_k \mid A \mid Pp_k) \ldots (s_n \mid Pp_n) = \\
&= \sum_P (-1)^P \sum_{k=1}^{n'} (s_1 \mid Pp_1) \ldots (s_k \mid A \mid Pp_k) \ldots (s_{n'} \mid Pp_{n'}) \ldots (s_n \mid Pp_n) + \\
&+ \sum_P (-1)^P \sum_{k=n'+1}^{n} (s_1 \mid Pp_1) \ldots (s_{n'} \mid Pp_{n'}) \ldots (s_k \mid A \mid Pp_k) \ldots (s_n \mid Pp_n) = \\
&= \sum_{P'} (-1)^{P'} \sum_{k=1}^{n'} (s_1 \mid P' p_1) \ldots (s_k \mid A \mid P' p_k) \ldots (s_{n'} \mid P' p_{n'}) \cdot \\
&\cdot \sum_{P''} (-1)^{P''} (s_{n'+1} \mid P'' p_{n'+1}) \ldots (s_n \mid P'' p_n) + \\
&+ \sum_{P'} (-1)^{P'} (s_1 \mid P' p_1) \ldots (s_{n'} \mid P' p_{n'}) \sum_{P''} (-1)^{P''} \sum_{k=n'+1}^{n} (s_{n'+1} \mid P'' p_{n'+1}) \ldots \\
&\ldots (s_k \mid A \mid P'' p_k) \ldots (s_n \mid P'' p_n) = \\
&= \langle S_a' \mid A \mid S_b' \rangle \langle S_a'' \mid S_b'' \rangle + \langle S_a' \mid S_b' \rangle \langle S_a'' \mid A \mid S_b'' \rangle
\end{aligned} \tag{A3}$$

Proof of the Theorem 3

According to eqs. (4)

$$\langle S_a \mid S_b \rangle = \sum_P (-1)^P (1 \mid P2) (3 \mid P4) \ldots (2n-1 \mid P\,2n) \tag{A4}$$

and

$$\langle S_a \mid A \mid S_b \rangle = \sum_P (-1)^P \sum_{r=1}^{n} (1 \mid P2) (3 \mid P4) \ldots (2r-1 \mid A \mid P\,2r) \ldots (2n-1 \mid P\,2n) \tag{A5}$$

1. Consider first the overlap $S_{ab} = \langle S_a \mid S_b \rangle$. In the relation (A4) the summation is performed over all permutations P of n indices $2, 4, 6, \ldots, 2n$. However, BO $\mid 1$) has a nonvanishing overlap only with BO's $\mid 2$) and $\mid 2n$) (see Figure 9a). Hence, either $P2 = 2$ or $P2 = 2n$. Consider first the case $P2 = 2$. This implies $P4 = 4$, since otherwise $(3 \mid P4) = 0$. Furthermore $P6 = 6$ etc.. Hence there is only one permutation satisfying $P2 = 2$ which leads to a nonvanishing term in (A4). This permutation is identity. Analogously, one finds that another possibility $P2 = 2n$ leads to a cyclic permutation of n indices $2, 4, \ldots, 2n$. This permutation has the parity $(-1)^{n+1}$ and hence

$$\langle S_a \mid S_b \rangle = (1 \mid 2) \ldots (2n-1 \mid 2n) + (-1)^{n+1} (1 \mid 2n) \ldots (2n-1 \mid 2n-2) = \\ = [1 + (-1)^{n+m+1}]/2^n \tag{A6}$$

where we have used relations (12). This proves point 1 of the above Theorem.

2. Consider now the matrix elements of elementary operators A^{kl}. According to Theorem 1. the normal phase between structures S_a and S_b does not depend on the particular representation satisfying normal ordering convention, as long as the partition on sink and source vertices is not changed. This option can be used in order to simplify the proof. In particular, a normal bond can be chosen to be the bond (1), cis-bridge can be chosen to connect vertex (1) with vertex (2n'), while trans-bridge can be chosen to connect vertex (1) with vertex $(2n' + 1)$ (sink-sink case), or vertex (2) with vertex $(2n' + 2)$ (source-source case).

a) Let $A = A^s$ be the normal bond operator and let bond (s) be bond (1) (see Fig. 9a). It follows $(2r-1 \mid A^s \mid P\,2r) = 0$ unless $2r - 1 = 1$. Hence

$$\langle S_a \mid A^s \mid S_b \rangle = \sum_P (-1)^P (1 \mid A^s \mid P2)\,(3 \mid P4) \ldots (2n-1 \mid P\,2n) \tag{A7}$$

In the above expression either $P2 = 2$ or $P2 = 2n$, since otherwise $(1 \mid A^s \mid P2) = 0$. The first possibility ($P2 = 2$) implies $P4 = 4$, this implies $P6 = 6$ etc., Similarly, for the case $P2 = 2n$. By iduction

$$\langle S_a \mid A^s \mid S_b \rangle = (1 \mid A^s \mid 2)\,(3 \mid 4) \ldots (2n-1 \mid 2n) + \\ + (-1)^{n+1} (1 \mid A^s \mid 2n)\,(3 \mid 2) \ldots (2n-1 \mid 2n-2) = (-1)^{\mathrm{Sgn}(s)} [1 + (-1)^{n+m+1}]/2^n \tag{A8}$$

where we have again used relations (12), and where (s) stands for bond (1). According to the above discussion the same relation holds for any normal bond (s). This proves point 3 of the above Theorem. The proof of point 2 can be done along the same lines and hence it will be omitted here.

b) Let $A = A^s$ be a cis-bridge operator and let bond (s) connect vertices (1) and (2n') as shown in Figure 9b. The matrix element $(2r-1 \mid A^s \mid P\,2r)$ in the expression (A5) equals zero, unless either $2r - 1 = 1$ or $2r - 1 = 2n' - 1$. Hence

$$\langle S_a \mid A^s \mid S_b \rangle = \sum_P (-1)^P (1 \mid A^s \mid P2)\,(3 \mid P4) \ldots (2n-1 \mid P\,2n) + \\ + \sum_P (-1)^P (1 \mid P2) \ldots (2n'-1 \mid A^s \mid P\,2n') \ldots (2n-1 \mid P\,2n) \tag{A9}$$

$(1 \mid A^s \mid P2) \neq 0$ implies $P2 = 2n'$, this implies $P4 = 2$ etc. Analogously, $(2n'-1 \mid A^s \mid P\,2n') \neq 0$ implies $P(2n') = 2n$, hence $P2 = 2$, since otherwise $(1 \mid P2) = 0$. Furthermore, $P4 = 4, \ldots, P(2n'-2) = 2n'-2$. Also $P(2n) = 2n-2$, since otherwise $(2n-1 \mid P\,2n) = 0$. Next $P(2n-2) = 2n-4, \ldots, P(2n'+2) = 2n'$. Hence

$$\langle S_a \mid A^s \mid S_b \rangle = (-1)^{n'+1} (1 \mid A^s \mid 2n')\,(3 \mid 2) \ldots (2n'-1 \mid 2n'-2)\,(2n'+ \\ + 1 \mid 2n'+2) \ldots (2n-1 \mid 2n) + (-1)^{n+n'} (1 \mid 2) \ldots (2n'-3 \mid 2n'-2)\,(2n'- \\ - 1 \mid A^s \mid 2n)\,(2n'+1 \mid 2n') \ldots (2n-1 \mid 2n-2) \tag{A10}$$

In the first term of the above expression there is a cyclic permutation of n' indices $2, 4, \ldots, 2n'$. Hence phase $(-1)^{n'+1}$. In the second term there is a cyclic permutation of indices $2n'+2, 2n'+4, \ldots, 2n$ $(n - n' + 1$ indices), hence phase $(-1)^{n+n'}$. Finally, using eqs. (12) and (13) one obtains

$$\langle S_a \mid A^s \mid S_b \rangle = (-1)^{n'+m'+1} [1 + (-1)^{n+m+1}]/2^n \tag{A11}$$

where (2n′) is the number of bonds in the cycle c′, while m′ is the number of excited BO's corresponding to this cycle. This proves point 4 of the above Theorem.

c) Let $A = A^s$ be a trans-bridge operator. Assume that bond (s) connects two sink vertices on the cycle G_{ab} as shown in Figure 9c. A matrix element $(2r - 1 \mid A^s \mid P\,2r)$ in the expression (A5) equals zero, unless $2r - 1 = 1$ or $2r - 1 = 2n' + 1$. Hence

$$\langle S_a \mid A^s \mid S_b \rangle = \sum_P (-1)^P (1 \mid A^s \mid P2)\,(3 \mid P4) \ldots (2n - 1 \mid P\,2n) + \\ + \sum_P (-1)^P (1 \mid P2) \ldots (2n' + 1 \mid A^s \mid P\,(2n' + 2)) \ldots (2n - 1 \mid P\,2n) \qquad (A12)$$

$(1 \mid A^s \mid P2) \neq 0$ implies $P2 = 2n'$. This implies $P4 = 2, \ldots, P\,(2n') = 2n' - 2$. Also $P\,(2n' + 2) = 2n' + 2$, since otherwise $(2n' + 1 \mid P\,(2n' + 2)) = 0$, etc. Analogously, in the second term $(2n' + 1 \mid A^s \mid P\,(2n' + 2)) \neq 0$ implies $P\,(2n' + 2) = 2n$. Hence $P\,(2n' + 4) = 2n' + 2, \ldots, P\,(2n) = 2n - 2$ and $P2 = 2$, $P4 = 4, \ldots, P\,(2n') = 2n'$. It follows:

$$\langle S_a \mid A^s \mid S_b \rangle = (-1)^{n'+1} (1 \mid A^s \mid 2n')\,(3 \mid 2) \ldots (2n' - 1 \mid 2n' - 2)\,(2n' + \\ + 1 \mid 2n' + 2) \ldots (2n - 1 \mid 2n) + (-1)^{n+n'+1} (1 \mid 2) \ldots (2n' - 1 \mid 2n')\,(2n' + \\ + 1 \mid A^s \mid 2n)\,(2n' + 3 \mid 2n' + 2) \ldots (2n - 1 \mid 2n - 2) \qquad (A13)$$

In the first term of this expression there is a cyclic permutation of n′ indices 2, 4, 6, . . ., 2n′. Hence phase $(-1)^{n'+1}$. In the second term there is a cyclic permutation of indices 2n′ + 2, 2n′ + 4, . . ., 2n. This gives the phase $(-1)^{n+n'+1}$. Finally, using eqs. (12) and (14) one obtaines

$$\langle S_a \mid A^s \mid S_b \rangle = (-1)^{n'+m'+1} [1 + (-1)^{n+m}]/2^n \qquad (A14)$$

This proves point 5 for the case when the trans-bridge (s) connects two sink vertices on the cycle G_{ab}. Analogously, one can derive the corresponding relations for the case when bond (s) connects two source vertices. This completes the proof for Theorem 3.

Proof of the Theorem 4

This Theorem can be proved along the same lines as the Theorem 3 (see Figure 9.). We start from eqs. (A4) and (A5) and then we treat each possible case in turn. One can, however, greatly simplify the proof if one considers an even chain to be derived from an even cycle by cutting it at some sink position. Each formula for a cycle usually contains two terms (see for example formulas (A6), (A8), (A10) and (A13)). If we cut a cycle we formally make either one of the overlaps $(2r - 1 \mid 2r)$ $(r = 1, \ldots, n)$ or one of the overlaps $(2r + 1 \mid 2r)$ $(r = 0, \ldots, n - 1)$ equal zero. In either case one of the two terms entering formulas (A6)—(A13) equals zero. Closer examination leads to formulas (20)—(24). This proves Theorem 4.

Proof of the Theorem 5

The first part of this Theorem is easy to prove. No overlap $(2r - 1 \mid P\,2r)$ in the expression (A4) can connect chains l_1 and l_2. Since those chains are odd, overlap $\langle S_a \mid S_b \rangle$ vanishes. Similarly, if A^{kl} is an internal operator then no matrix element $(2r - 1 \mid A^{kl} \mid P\,2r)$ in the expression (A5) connects chains l_1 and l_2. Hence matrix element $\langle S_a \mid A^{kl} \mid S_a \rangle$ vanishes. In the case of external operators we again use a helpful device. From Figure 11. and in connection with eq. (A5) it follows $P2 = 2$, $P4 = 4, \ldots$ and $P\,(2n) = 2n$, $P\,(2n - 2) = 2n - 2, \ldots$ This holds true along both chains l_1 and l_2 up to the points where the bond (s) is situated (Figures 10b and c). Now at this point the bond (s) should be taken into account since it enters the matrix element $(2r - 1 \mid A^s \mid P\,2r)$. If we proceed along chains l_1 and l_2 we can see that this implies overlaps $(2t + 1 \mid 2t)$ and $(2t + 3 \mid 2t + 2)$, i. e. overlap $(2t + 1 \mid 2t + 2)$ does not occur. But this means that one can identify terminal source vertices of

the two chains, without changing the matrix element $\langle S_a | A^s | S_b \rangle$. Hence formulas (23) and (24) derived for an even chain are also valid for the case of two odd chains, provided terminal source vertices of those two chains are identified (Figures 10b and c).

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SAŽETAK

Novi semiempirijski pristup proračunu elektronske strukture π-elektronskih sustava, I. Matrični elementi

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Predlaže se novi semiempirijski pristup za proračun elektronske strukture π-elektronskih sustava. Metoda sadržava neke karakteristike i VB i MO teorije. Iz VB teorije zadržan je pojam rezonancije, dok je svaka pojedinačna veza tretirana na MO način. U radu se izvode matrični elementi prekrivanja i jednočestičnih operatora među rezonantnim strukturama definiranim na nov način.